Complex Absorbing Potentials (CAP) [7,8] are particularly straight forward and simple to implement in the post-Hartree-Fock methods. The essential idea underlying the CAP for calculating resonances is to introduce an absorbing boundary condition in the exterior region of the molecular scattered target which results in a non-hermitian Hamiltonian. One of the square integrable eigenfunctions of this Hamiltonian corresponds to the resonant state. The associated complex eigen-value then gives the position and width of the resonance or the auto-ionizing state. The CAP procedure is simple to implement within the electronic structure methods since the internal structure of the physical Hamiltonian is not affected and there is no need to use other basis sets than usual real Gaussians. Thus many existing electronic structure calculations for bound states of molecule can easily be adapted for the resonance study.

Since study of resonance states involves study of metastable (N+1) particle system. The electron correlation and relaxation effects are clearly crucial factors in the formation and decay of the metastable state [9]. The accuracy of the effective one-particle based approximations in the case of an electron scattering resonance depends on the extent to which the electron correlation is important in the description of a particular state. CAP potentials have been applied to the molecular resonances in the context of configuration interaction (CI) [10] and electron propagator theories [11–13] and coupled-cluster (CC) based methods [14,15]. The ionization potential/electron affinity studies provide the simultaneous calculation of both energy [real part] and width [twice the imaginary part] of electron detachment Auger resonance [$E_0^N - E_s^{N-1}$] and electron attachment shape resonance [$E_s^{N+1} - E_0^N$], where s labels a stationary state and E_0^N is the ground state total energy of the neutral N-electron target. For atomic and molecular systems, the CC formalism leads to significantly improved accuracy and is generally regarded as the best scheme that is presently available. The Fock space multi-reference coupled-cluster (FSMRCC) method [16–18] has been quite successful in the calculation of electron affinity and ionization potential [19]. Coupled-cluster based methods, with exponential wave-operator, includes dynamic electron correlation efficiently and in a size-extensive manner. The FSMRCC provides with the direct difference energies.

The analytically continued effective Hamiltonian are obtained by solving the Bloch equation. In principle, the analytically continued effective Hamiltonian can be constructed in a brute-force manner as in the conventional FSMRCC methods by solving the nonlinear amplitude equations iteratively. This is the method we adopt in the CAP-FSMRCC approach. In this approach the electron correlation, relaxation and the analytic continuation are treated together. Instead of doing so, however, in the CIP-FSMRCC method, we apply analytical continuation over an already correlated effective Fock space Hamiltonian. One may have to solve a new set of nonlinear amplitude equations for the complex Fock space cluster amplitudes. At the converged limit both the methods should give the exact eigen-values. In CAP-FSMRCC we vary the CAP

strength (η) and solve the effective Hamiltonian for each η values for checking the convergence of the eigen-values in the complex plane. This leads to the η trajectory generation. The η trajectory generation is computationally demanding as one has to solve the full FSMRCC problem for each η value. In CIP-FSMRCC analytical continuation scheme is defined over an already correlated cluster amplitudes. This approximation does not lead to any serious error in calculation of resonance energy. In this paper we study the shape resonance in e^-–H_2CO and e^-–CO scattering.

Calculations presented are limited to single and double excitation operators. Section 2 a gives brief introduction for CAP in FSMRCC method. Section 3 contains discussion of our results. The results are compared with experimental results as well as those obtained using other theoretical approaches.

2. Theoretical background

In this section we briefly discuss the Fock space or valence-universal CC theory for resonance problem. With the complex absorbing potentials, FSMRCC has been used to calculate the shape resonances in electron-atoms/molecule collisions [14,15]. The CAP-FSMRCC method provides direct access to the energy difference $(E_s^{N+1} - E_0^N)$, where E_0^N is the ground-state energy of the neutral N-electron target at the same geometry. Both static and dynamic electron correlation in the N- and $(N+1)$-electron systems are treated in a consistent manner in this approach.

In the CAP treatment of electronic resonance states, electron absorption is accomplished by replacing the molecular Hamiltonian H by

$$H(\eta) = H - i\eta W \tag{1}$$

where η is a real, non-negative number referred to as CAP strength parameter. W is a local, positive semi-definite one-particle operator. In the limit $\eta \to 0^+$, $H(\eta)$ defines an analytical continuation of H. The valence universal operator $\Omega(\eta)$ takes the model space $\Psi_\mu^{(1,0)}$ to the exact wavefunction of the analytically continued Hamiltonian. The wave-operator Ω can be expressed as

$$\Omega(\eta) = \{e^{T^{(1,0)}(\eta)}\} \tag{2}$$

where, the curly bracket denotes the normal ordering of the operator in it. The exact (1,0) sector eigenfunctions of the CAP perturbed Hamiltonian can be written in the Fock space method using Lindgren's normal-ordered ansatz [17] as

$$\Psi_\mu^{(1,0)}(\eta) = \Omega(\eta)\Psi_\mu^{0(1,0)} \tag{3}$$

The perturbation due to the CAP is incorporated while correlating the target. Hence the wave-operator and the cluster operators will be complex, while the vacuum corresponds to the Hartree-Fock ground state of the N-electron system without the CAP. In general, the wave-operator for the Fock space of m active particles and n active holes correlates

all lower active particle-active hole Fock space sectors and thus is valence universal in nature. For the specific (1,0) sector of Fock space, the wave-operator can be written as

$$\Omega(\eta) = \left\{ e^{T^{(0,0)}(\eta)+T^{(1,0)}(\eta)} \right\} \tag{4}$$

where $T^{(0,0)}(\eta)$ is the cluster operator for the single reference coupled cluster case, containing only hole-particle excitation operators. In this case, however, due to the CAP, the $T^{(0,0)}(\eta)$ amplitudes will be complex. The $T^{(1,0)}(\eta)$ operator destroys exactly one active particle and is also complex.

The normal ordering of the wave-operator prevents the different T operators to contract among themselves and leads to a decoupling of the Bloch equations for different sectors. Equations for cluster amplitudes for different sectors can be solved using the subsystem-embedding-condition (SEC) *i.e.*, first the equations for the lowest sectors are solved and with the T operators of the lower sectors as constants, equations for higher Fock space sectors are solved progressively upwards. The Bloch equations for the (1,0) sector can be written as

$$P^{(m,n)}H(\eta)\Omega(\eta)P^{(m,n)} = P^{(m,n)}\Omega(\eta)H_{\text{eff}}(\eta)P^{(m,n)} \forall m = 0,1 \qquad \forall n = 0 \tag{5a}$$

$$Q^{(m,n)}H(\eta)\Omega(\eta)P^{(m,n)} = Q^{(m,n)}\Omega(\eta)H_{\text{eff}}(\eta)P^{(m,n)} \forall m = 0,1 \qquad \forall n = 0 \tag{5b}$$

where

$$H_{\text{eff}}(\eta) = P^{(m,n)}\Omega(\eta)^{-1}H(\eta)\Omega(\eta)P^{(m,n)} \forall m = 0,1 \qquad \forall n = 0 \tag{5c}$$

is an effective Hamiltonian whose eigenvalues determine the roots of the Fock space sector (1,0) :

$$H_{\text{eff}}(\eta)C(\eta) = C(\eta)E(\eta)\,. \tag{6}$$

The symbols $P^{(m,n)}$ and $Q^{(m,n)}$ used in the above equations denote the projection operator for the (1,0) sector of model space and its complementary space, respectively. The simplest approach to get the resonance energy in FSMRCC framework is to introduce the CAP at the SRCC level to generate the intermediate one-body operator $\bar{F}(\eta)_N$ and two-body operator $\bar{V}(\eta)_N$ to get the $T^{(1,0)}(\eta)$ amplitudes. This makes the cluster amplitudes at each sector complex and hence the energies obtained are also complex. This also implies that we solve the CC for each value of the η cap potential strength. This is very time consuming. Based on the formulation of correlated independent particle potential by Bartlett and co-workers [20] Sajeev *et al* [21,22] proposed the method for the calculation of the resonant energies using correlated complex independent potential (CIP). Sajeev *et al* [21] implemented the approximation in which the CAP was introduced directly in the effective Hamiltonian to obtain the complex energies. This approximation has been tested and gives reliable results for

shape resonance. For the CAP-FSMRCC the analytic continuation scheme starts from the definition of the many-body Hamiltonian and the diagonalization of the complex effective Hamiltonian yields the resonance energy relative to the target state, while for the CIP-FSMRCC the analytic continuation scheme starts from the real FSMRCC effective Hamiltonian and the diagonalization of the iteratively solved new complex effective Hamiltonian yields an equivalent energy difference. For detailed working equations see Ref. [21].

3. Results and discussion

In this paper we report $^2B_1$ shape resonance in e^-–H_2CO and $^2\Pi$ shape resonance for e–CO. The electronic configuration of formaldehyde in its ground state is $[\text{core}]\,4a_1^2 1b_2^2 5a_1^2 1b_1^2 2b_2^2$. The ground state of the negative ion is formed by addition of electron in the $2b_1$ orbital. This π^* orbital is largely localized on the C=O bond in an antibonding manner. This leads to increase in bond length of the anion compared to that of the neutral molecule [23]. The polarity of the C=O group indicates that long range polarization will be important and hence appropriate basis with sufficient diffuse p functions and d functions are required. Basis set used for both the molecules is double zeta basis for carbon and oxygen augmented with four p type and one d function. The $\{\alpha(p) = 0.0382, 0.01232, 0.004107, 0.001325; \alpha(d) = 0.0635\}$ on carbon, $\{\alpha(p) = 0.0689, 0.0222, 0.00717, 0.000746; \alpha(d) = 1.211\}$ on oxygen and one p type function $\{\lambda(p) = 0.07\}$ on hydrogen atom were used. In this paper we report the $^2B_1$ shape resonance in the electron formaldehyde scattering using complex coupled cluster method. The C=O π^* orbital is the resonant orbital of formaldehyde. The resonances are identified by plotting the complex electron affinity as a function of η (η trajectory) for box sizes near the optimal values and the quasi-stable region in the trajectory is associated with resonance energy (real part) and half width (imaginary part). First, to calculate the optimum box size for which the absorbing potential is best adapted to the basis set and the size of the target system, CIP-FSMRCC calculations were performed for various CAP-box sizes. The optimum value of box size is found to be $c_x = c_y = 9.0$ au, $c_z = 9.5$ au. The values of the energy and width obtained by various theoretical [24,25] and experimental [26,27] methods, are shown in Table 1. Comparing the results with Diagonal 2ph TDA we find that CC gives position of the resonance energy smaller where as the width is slightly larger. The complex Kohn variation method [24] for fixed geometry predicts resonance at 1.0 eV with the width of 0.5 eV. Our results give shorter width and position compared to the complex Kohn method. It is known that the position of the resonance is sensitive to the target distortion effects. Also, electron attachment in antibonding orbitals result in narrow widths with stretching of the bond involved in the resonance formation *i.e.* stretching of C=O. It may be interesting to study the resonance as a function of C=O bond distance with the inclusion of correlated static exchange potential.

Table 1. Resonance energy and width of the $^2B_1$ H_2CO^- shape resonance.

Method	Energy(eV)	Width (eV)
Electron transmission[a]	1.0 /0.86	–
Vibrational excitation[b]	0.87	–
Theory		
Complex Kohn[c]	1.0	0.5
Dilated electron propagator[d]		
Zeroth order	1.00	0.10
Quasi-particle second order	0.99	0.10
Quasi particle 2ph-TDA	0.98	0.11
Diagonal 2ph-TDA	0.89	0.12
2nd order	0.89	0.09
CIP-FSMRCC	0.76	0.32

(a) Ref [26], (b) Ref [27], (c) Ref [24], (d) Ref [25]

Table 2. Resonance energy and width of the $^2\Pi$ CO^- shape resonance.

Method	Energy(eV)	Width (eV)
CIP-FSMRCC	1.47	0.34
Bi-variational SCF[a]	1.71	0.10
Expt[b]	1.50	0.40

(a) Ref. [29], (b) Ref [28]

For carbon monoxide we have used the same basis as before. The RHF wavefunction for CO is $[\text{core}]\sigma_{2s}\sigma^*_{2s}\pi_{2p}\sigma_{2p} \mid \pi^*_{2p}$. In CO π^*_{2p} is the resonating orbital. The optimum value of box size was found to be $c_x = c_y = c_z = 10.0$ au. We obtained the resonance energy of 1.47 eV using CIP-FSMRCC and the corresponding width is 0.34 eV. The experimental resonance energy is 1.5 eV and width is 0.4 eV. Our results for the resonance energy are quite close to the experimental values [28]. Using the bi-variational SCF Mishra and co-workers obtained resonance energy of 1.71 eV with 0.1 eV as width in a 4S5P basis. Though bi-variational SCF [29] can isolate the LUMO as the potential resonant orbital and provide reasonable picture of the metastable attachment, the narrow width could result due to inadequate treatment of electron correlation.

Acknowledgment

Grant from Department of Science and Technology (DST) India is acknowledged.

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